Sains Malaysiana 42(4)(2013): 449–457

Rigid Polyurethane Foam from Glycolysed Polyethylene Terephthalate Dissolved in Palm-based Polyol

(Busa Poliuretana Tegar daripada Sisa Polietilena Tereftalat Terglikolisis Terlarut Poliol Sawit)

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ABSTRACT

An investigation on the thermal and mechanical properties of rigid polyurethane (PU) foam from polyethylene terephthalate (PET) waste (of plastic drinking bottles) was conducted. The PET waste was glycolysed with ethylene glycol prior to blending with palm based-polyol (PKO-p). This blend was then reacted with 2, 4-methylene diphenyl diisocyanate (MDI) at a ratio of 1:1 to form the PU foam. The incorporation of the glycolysed PET (g-PET) into the PKO-p was studied at 50, 70 and 100% w/w loading. PU foam prepared from 100% w/w g-PET (without PKO-p) resulted in PU with high glass transition temperature and mechanical strength. This water-blown foam has molded and core densities of 182 kg m^{-3} and 179 kg m^{-3}, respectively, with maximum compressive stress and modulus at 396 kPa and 1920 kPa, respectively. An initial enthalpy value of 3164.8 cal g^{-1} and a glass transition temperature of 65°C were observed.

Keywords: Glycolysis; palm based-polyol; polyethylene terephthalate waste; rigid polyurethane foam

ABSTRAK

Suatu kajian tentang sifat terma dan mekanik busa tegar poliuretana (PU) daripada sisa polietilena tereftalat (PET) (botol plastik minuman) telah dijalankan. Sisa PET ini telah diglikolisiskan sebelum diadun bersama poliol sawit (PKO-p). Adunan ini kemudiannya ditindak balaskan dengan 2, 4-metilena difenil diisosianat (MDI) pada nisbah 1:1 untuk menghasilkan busa PU. Kemasukan PET terglikolisis (g-PET) ini ke dalam PKO-p dikaji pada penambahan 50, 70 dan 100% bt/bt. Busa PU yang disediakan daripada 100% bt/bt g-PET (tanpa PKO-p) menghasilkan PU yang mempunyai suhu peralihan kaca dan kekuatan mekanik tertinggi. Busa yang disediakan dengan agen pembusaan air ini mempunyai ketumpatan teracu dan teras masing-masing 182 kg m^{-3} dan 179 kg m^{-3} dengan tegasan dan modulus mampatan maksima pada masing-masing 396 kPa dan 1920 kPa. Nilai entalpi awal 3164.8 kal g^{-1} dan suhu peralihan kaca pada 65°C direkodkan.

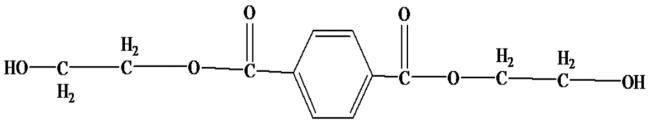
Kata kunci: Busa poliuretana tegar; glikolisis; poliol sawit; sisa polietilena tereftalat

INTRODUCTION

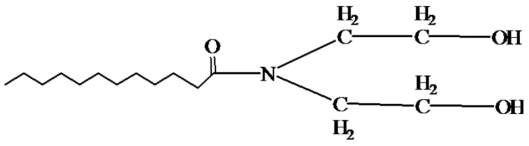
Polyurethane (PU) is a copolymer formed by polyaddition reaction of isocyanate with polyol resin (Lee & Ramesh 2004). The reaction of isocyanate with active hydroxyl functional group produces urethane linkage (Liang & Shi 2010). Polyurethane foam has been widely utilized in the appliances and construction industry because of its excellent thermal insulation and mechanical properties (Bartha et al. 2011). For decades, polyols used in polyurethane industry are petrochemical-based where petroleum oil is used as the starting raw material (Badri et al. 2004). However, this rapidly diminishing resource (Chuayjuljit et al. 2007) is expensive due to high depleting rate and high production costs. Thus, considerable attention has been devoted to synthesis of PU polyol from palm kernel oil (Badri et al. 2000, 2001, 2004) as one of the alternatives.

Recycling poly(ethylene terephthalate) (PET) waste is of interest to many researchers particularly by chemical approach to convert high molecular weight polymers into low molecular weight substances (Awaja & Pavel 2005; Limpiti & Potiyaraj 2009). PET can be depolymerized into smaller molecules via glycolysis in excess glycols. The components of the glycolysed products depending on the type of glycol being used, are predominantly monomers and oligomers of bis(2-hydroxylethyl) terephthalate (BHET) (Abdelaal et al. 2011; Imran et al. 2010). Glycolysed products have the potential as starting materials for synthesis of other polymers with higher economic values, such as the production of unsaturated polyester resins, for the making of PU foam (Vaidya & Nadkarni 1988) and urethane oils (Saravari et al. 2004).

BHET (Figure 1 (a)) is of interest due to the presence of two active primary hydroxyl groups which contributes to higher reactivity (Lee & Ramesh 2004), thus prone to react with isocyanate to produce urethane linkages. Meanwhile, aromatic rings which are located at the centre of BHET chemical structure contribute to rigidity and hardness to the polymeric chain and foam structure. Palm based-monoester (Figure 1(b)) derivatised from palm kernel oil (MY 145094-A) has two active hydroxyl groups bonded to the nitrogen atom. These monomers were blended to form the resin and reacted with 2, 4-methylene diphenyl diisocyanate (crude MDI) to produce PU.



(a)



(b)

FIGURE 1. Structure of (a) bis(2-hydroxyethyl terephthalate) (BHET) and (b) palm based monoester

This paper foreseen the potential of BHET as a monomer in the preparation of polyurethane foam. Its mechanical and thermal properties were determined. Since BHET is a white solid at room temperature, palm based-monoester was used as a solvent to dissolve it. Incorporation of BHET provides another approach for varieties in the properties of PU foam.

EXPERIMENTAL METHODS

MATERIALS

Clear post-consumer PET soft drink bottle collected from plastic bottle recycle bin was ground into small pieces (6 mm × 3 mm) using Cheso Machinery Pte. Ltd. grinder model TSC-50. Ethylene glycol (99%) was obtained from Systerm Sdn Bhd. Zinc acetate (99.5%) was supplied by Analar. Silicone surfactant (Niax L5440) (manufactured by Witco Ltd. Singapore), tetramethylhexanediamine (TMHDA), pentamethylhexanediamine (PMDETA) and crude MDI (2, 4-methylene diphenyl diisocyanate) were obtained from Cosmopolyurethane (M) Sdn. Bhd., Port Klang, Malaysia. The palm-based monoester (PKO-p) was generously supplied by UKM Technology Sdn Bhd manufactured at its pilot reactor in MPOB-UKM Station, Pekan Bangi Lama, Malaysia. All the chemicals were used without further purification.

METHOD

GLYCOLYSIS OF PET BOTTLE

PET scrap was initially immersed in 1% (w/v) sodium hydroxide solution for 1 h to remove surface impurities and subsequently rinsed with water and dried in an oven at 80ºC (López-Fonseca et al. 2010). The pre-washed PET and ethylene glycol (EG) at a ratio of 1:4 (w/w)) in the presence of 0.5% (w/w) zinc acetate were glycolysed in a 1 L four-necked round bottom flask. The reaction was carried out under reflux in nitrogen gas atmosphere at 190°C for 8 h, following the methods suggested by Mosadeghzad et al. (2009). Upon completion of reaction, the glycolysed products (*g*-PET) were let to cool and stored in a screw cap glass jar.

PREPARATION OF POLYURETHANE FOAM

The resin was prepared by blending 90 g PKO-p, 10 g glycerol, 3 g surfactant, 5 g water, 0.3 g TMHDA and 0.15 g PMDETA using an overhead mechanical stirrer at 200 rpm for 5 min to obtain a homogenous resin. This resin was reacted with MDI at a ratio of 1:1 and was stirred vigorously at 1000 rpm for 10 s. The resin was instantaneously poured into a closed mold. The foam was demolded after 15 min and was allowed to condition at room temperature for 16 h before further characterization. This PU foam was treated as the control PU foam. The same experimental procedure was repeated by replacing the PKO-p with *g*-PET and a mixture of PKO-p with *g*-PET at various loading percentage of 50% w/w *g*-PET, 70% w/w *g*-PET and 100% w/w *g*-PET.

CHARACTERIZATION OF THE PKO-P, G-PET AND PU FOAM

FT-IR spectrum was recorded by computer interfaced with diamond attenuation total reflectance (DATR)-FTIR Perkin Elmer spectrum GX spectrometer. The sample was analysed within the wave number ranging from 4000 cm^{-1} to 650 cm^{-1} with a scanning resolution of 4 cm^{-1}. The core density was calculated following BS4370: Part 1: 1988 Method 2 using the equation of mass, kg divided by volume, m^3. The samples were cut using a handsaw into cubes of 50 mm × 50 mm × 50 mm in dimension. Three samples were used and were carefully weighed using an analytical balance. The dimensions were measured following BS4370: Part 1: 1988 Method 1B, using a digital Vernier caliper. The apparent moulded density was determined by the same method but without trimming off the outer part (skin) of the foam. The compressive strength test was carried out on a universal tensile machine model Instron series 2716 following BS4370: Part 1: 1988 Method 3. The foam samples were cut into cubes of 50 mm × 50 mm × 50 mm dimension. The

foam rise directions were marked and a crosshead speed of 10 mm/min was applied. The foam was compressed to 10% of its original thickness. The compression stress and modulus were recorded as average of five readings. Bomb calorimeter model PARR 6100EF jacket bomb calorimeter were used to determine the initial enthalpy value of PU foam, based on ASTM D5468-02 (2007) (standard test method for gross calorific and ash value of waste materials). Differential scanning calorimetry (DSC) was performed on a DSC 822 Model Mettler Toledo to observe the glass transition temperature, T_g of the PU foam. The samples with mass of 3 to 5 mg were analyzed in the temperature range of 30-250ºC at a heating rate of 10ºC min^{-1} under nitrogen gas atmosphere at a flow rate of 20 mL min^{-1}.

Results and Discussion

FTIR Spectroscopy Analyses of PKO-P and G-PET

The derivative of PET (*g*-PET) is a white sticky solid at room temperature while PKO-p is a golden yellow liquid at room temperature. The functional groups presence in PKO-p, *g*-PET and PU foam were verified by FT-IR spectroscopy analyses and compared with literatures (Badri et al. 2000; Mosadeghzad et al. 2009).

In this study, glycolysis of PET was carried out according to a method suggested by Mosadeghzad et al. (2009) and the FT-IR spectra of *g*-PET obtained from this study was compared (Figure 2). Figure 2 shows the absorption peak at 3423 cm^{-1} due to OH group (inter molecular hydrogen bonding), 2882-2951 cm^{-1} of C-H stretching, 1718 cm^{-1} of ester carbonyl group (C=O), 1,111 cm^{-1} of asymmetrical C-O-C stretching and 727-881 cm^{-1} indicating C-H aromatic ring (Mosadeghzad et al. 2009). There was no significant difference in peaks except for the intensity which might be due to reaction time and temperature of the glycolysis. These parameters were able to influence the degree of degradation, producing different type and amount of oligomers.

According to Wong and Badri (2010), synthesis of PKO-p through esterification of palm kernel oil and polyhydric compounds were monitored through the presen of hydroxyl group (OH) at 3391 cm^{-1}, ester carbonyl (C=O) at 1740 cm^{-1}, carbamate group (C-N) at 1622 cm^{-1} and alkane (C-H) at 2924 cm^{-1} and 2854 cm^{-1}, respectively. Figure 3 shows the FT-IR spectrum of the PKO-p.

FTIR Spectroscopy Analysis of the PU Foam

Figure 4(a) to 4(d) represents the FT-IR spectra of PU foams with 0%, 50%, 70% and 100% *g*-PET. According to Wong and Badri (2010), the functional groups in polyurethane can be detected through the existence of amide (-NH) stretching vibration at 3841 cm^{-1}, urethane carbonyl (C=O) at 1736 cm^{-1}, $-CH_2$ at 2927 cm^{-1}, -CNH at 1523 cm^{-1} and C-O-C at 1218 cm^{-1}.

Mechanical Properties of the PU Foam

Molded and Core Densities of PU Foam

Figure 5 shows the trend in molded and core densities of the prepared PU foam. Core density is the density of the foam without its skin. PU foam comprised of 100% *g*-PET has the highest molded and core densities at 182 $kg.m^{-3}$ and 179 $kg.m^{-3}$, respectively. On the other hand,

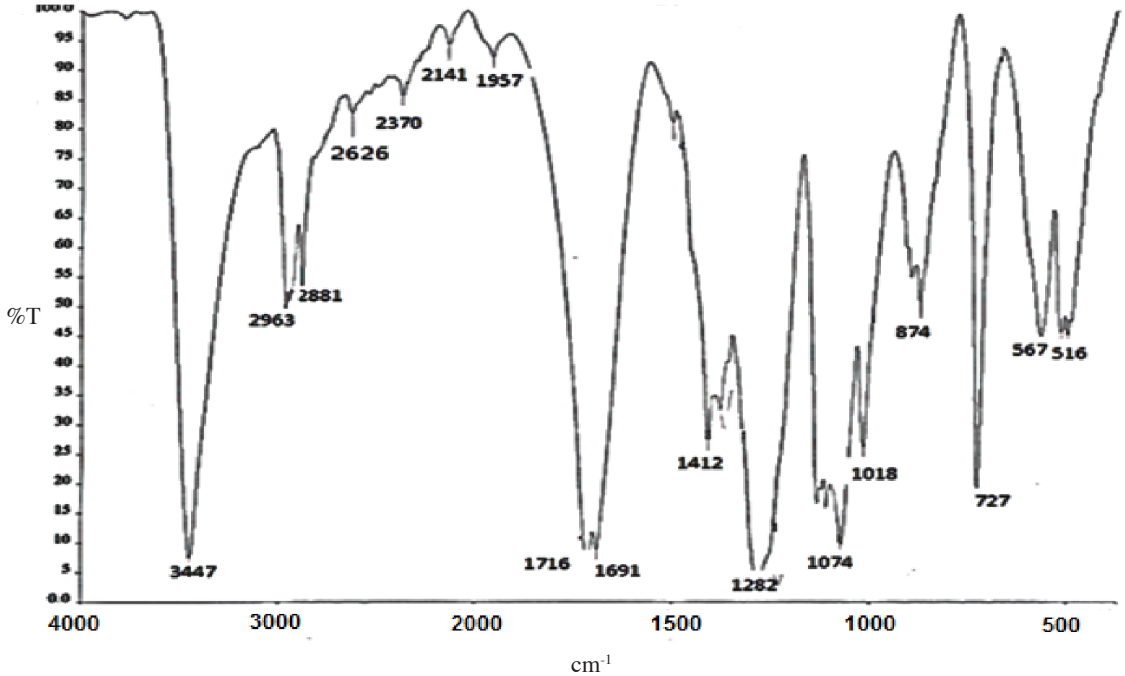


FIGURE 2. FT-IR spectrum of *g*-PET

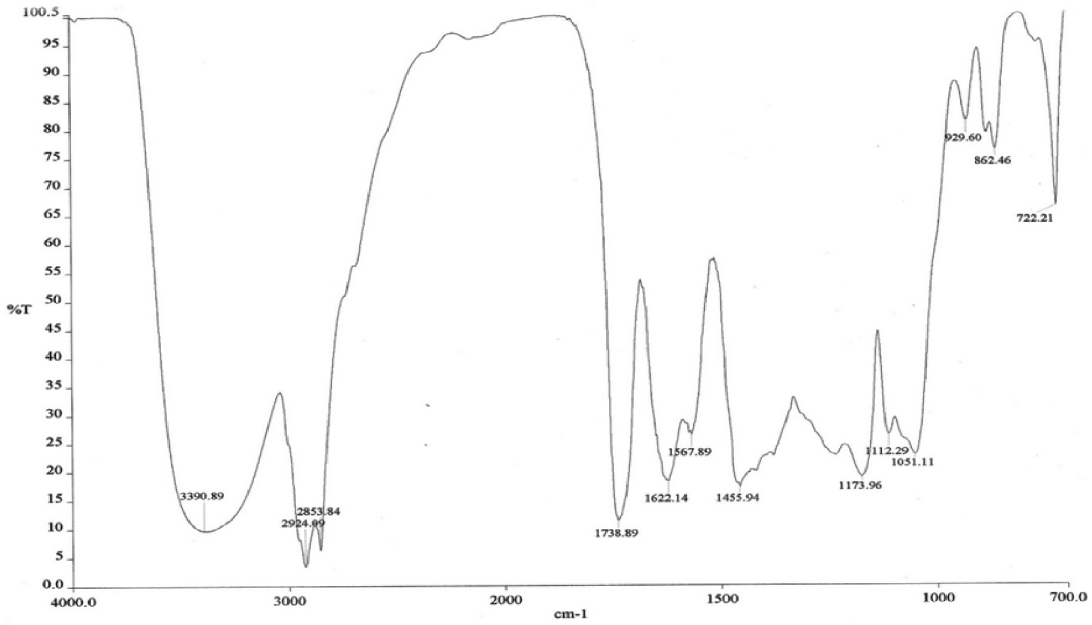
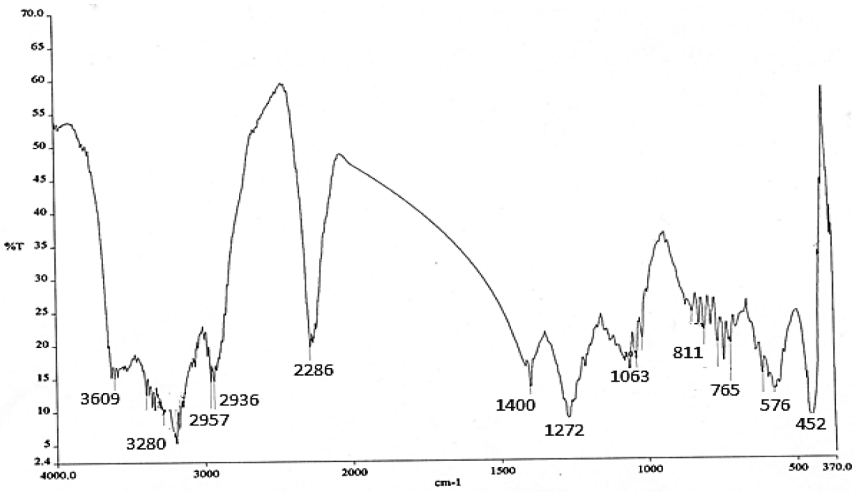


FIGURE 3. FT-IR spectrum of PKO-p



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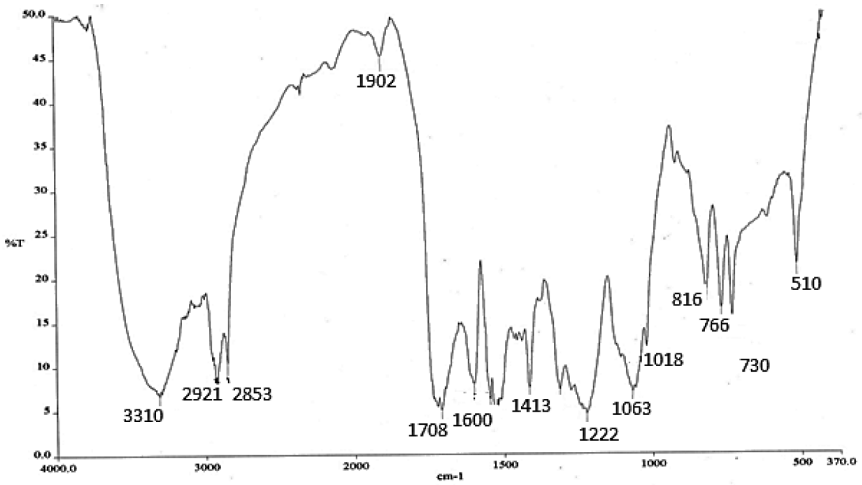

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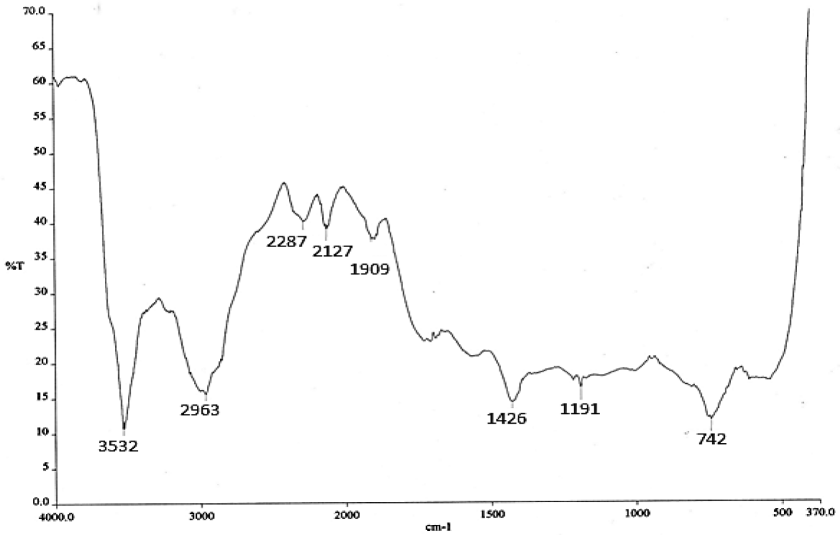

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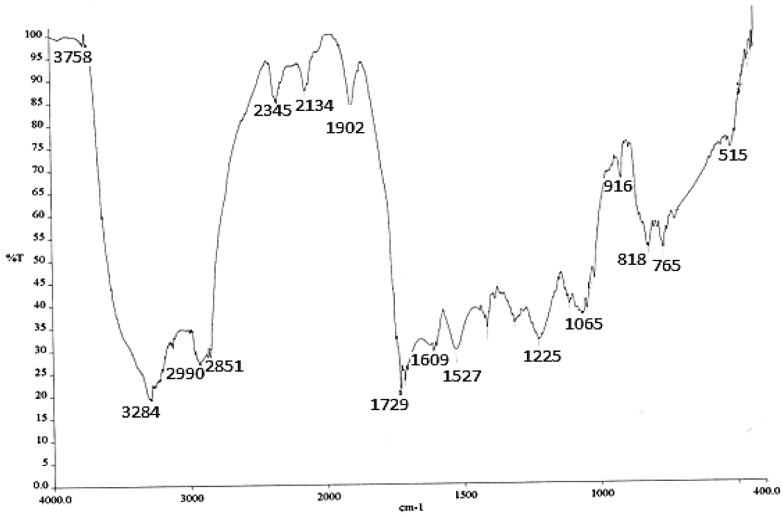

(d)

FIGURE 4. FTIR spectra of PU foam with (a) 0% *g*-PET (or 100% PKO-p), (b) 50% *g*-PET, (c) 70% *g*-PET and (d) 100% *g*-PET

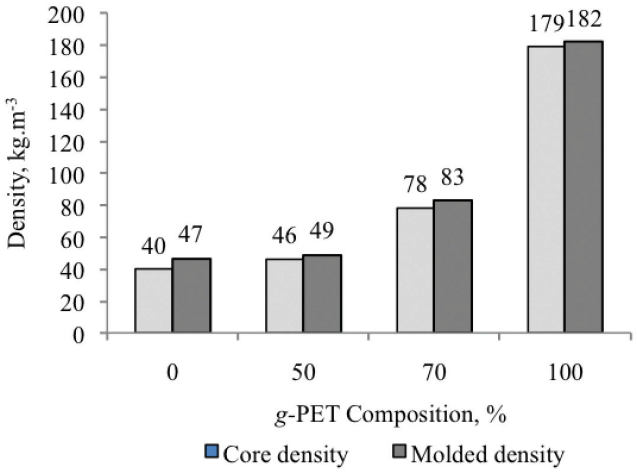

FIGURE 5. Molded and core densities of PU foam with the addition of 0, 50, 70 and 100% w/w *g*-PET

PU foam consisted of 0% *g*-PET (or 100% PKO-p) has the lowest molded and core density which is 47 kg.m^{-3} and 40 kg.m^{-3} , respectively. Higher composition of *g*-PET in the PU system resulted in higher foam's density. PKO-p is more hygroscopic than *g*-PET oligomers. Free water molecules have the tendency to bond with PKO-p more than *g*-PET. Water acts as a blowing agent during polymerization and releases carbon dioxide that helps in the foaming process. Formation of cellular structure during foaming process has a strong correlation with density. According to Matuana et al. (1998), the toughness of cell wall is influenced by average cell size of cellular structure. Nevertheless, the difference in core and molded densities were not significant indicating a uniform nucleation during foaming. This was later supported by data obtained from the compression test.

COMPRESSION STRENGTH

PU foam is capable of absorbing load stress when forces are exerted due to the present of cellular structures. It can absorb load stress from constant imposed load. Compression test was carried out in the foam rise direction. Since this property depends on the cell shape and size, the thickness of the foam is the major part that is of concern (Badri et al. 2005). According to Zollner and Bock (1993), compressive strength is twice higher and modulus is three times higher when load is imposed from foam rise direction compared with the side of foam rise direction. Compression strength of PU foam with different percentage of *g*-PET is shown in Figure 6.

Based on Figure 6, PU foam containing 100% *g*-PET has the highest compression strength and modulus at 396 kPa and 1920 kPa, respectively. Control PU foam made up of 100% PKO-p has the lowest compressive strength and modulus at 122 kPa and 127 kPa, respectively. Increased of stress is proportional to modulus. An increase in the content of *g*-PET increased the compressive strength of the PU foam. The same trend was observed in relation to the density of the PU foam. An increase in the foam density increased the foam strength as discovered by Lin (1997) when studying commercial foamed plastics.

Cowie (1991) suggested that degree of crosslinking in a polymeric system increased the density of a polymer. *g*-PET was capable of creating crosslinking due to the presence of OH groups and undergone random polymerization with PKO-p and MDI. Crosslink is one of the essential components which ascertain the hardness and stiffness of a polymer. A crosslinker has the ability to develop cellular network in the matrix. When forces are applied onto the polymer, the cellular structure is compacted and the stress is spread throughout the matrix uniformly. However, if cells are present due to mixing or voidages, failure for stress transfer is observed. The force will then concentrate around the ruptured cells (Badri et al. 2005). Compression modulus reflected the ability of a polymer to absorb applied force. Higher stress resulted in higher compressive modulus. According to Rivera-Armenta et al. (2004), high modulus indicated great ability to absorb energy.

THERMAL ANALYSIS OF POLYURETHANE FOAM

Thermal stability of a material reflected the ability of its chemical structure to resist chain termination and chain movement which were caused by heat. One of the important variables which control the thermal stabilization of a polymer is the basic material which made up the foam that is the polyol and isocyanate.

BOMB CALORIMETRIC ANALYSIS

Bomb calorimetry reflected the initial enthalpy value of a sample. According to Brady and Senesse (2004), initial

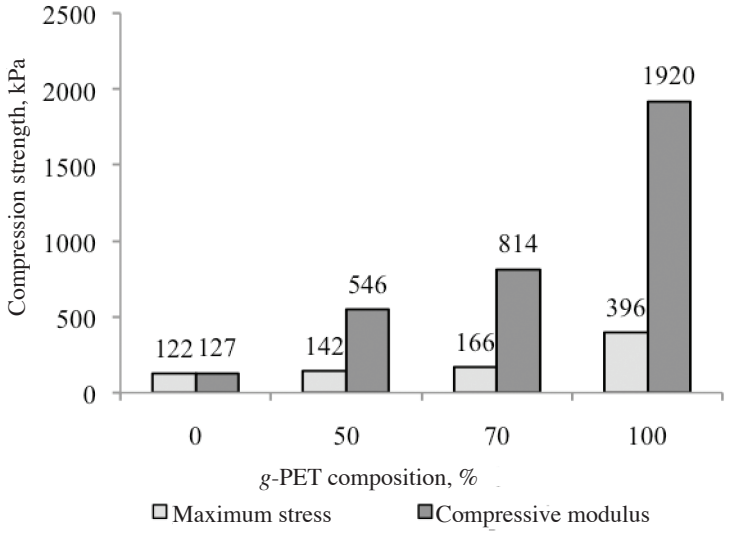

FIGURE 6. Compression strength and modulus of the PU foam with the addition of 0, 50, 70 and 100% w/w *g*-PET

enthalpy refers to the quantity of heat contained in a system which emancipate in energy form. From the observation, the highest enthalpy value was observed on sample using 100% *g*-PET at 3164.8 cal g^{-1} as shown in Figure 7. The lowest enthalpy (2042 cal g^{-1}) was observed for 100% PKO-p containing PU foam. This was attributed to the fact that more energy was required to break the bond in PU containing random blocks/segments consisted of the MDI, PKO-p and *g*-PET. These monomers formed the hard and soft building blocks in a random sequence.

DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSIS

Glass transition temperature of a polymer is strongly affected by arrangement and nature of hard and soft segments that build up the molecular structure of the polymer (Jung et al. 2000). Tawa and Ito (2006) discovered that the presence of soft segment in the hard domain lowered the glass transition temperature of the hard domain, consequently affecting the mechanical strength. However, this phenomenon is depending on the chain length of the soft segment. Generally, a multiphase polymer has more than one glass transition temperature as every phase has a different T_g. Generally, two-phase thermoplastic elastomer has a soft-segment T_g at a temperature below room temperature and hard-segment T_g at a temperature above room temperature. Thus the thermal property of a thermoplastic elastomer at low and high temperatures is depending on the soft and hard segment boundaries, respectively (Zollner & Bock 1993).

Figure 8(a) exhibits DSC thermograms of the PU foam with the addition of 0, 50, 70 and 100% w/w *g*-PET with extracted data of glass transition temperature, T_g as plotted in Figure 8(b). The highest T_g was recorded for PU foam containing 100% *g*-PET at 65.0°C in comparison with PU foam containing 100% PKO-p at 62.5°C. PU foam comprised of PKO-p and *g*-PET blends exhibited lower T_g than PU foam with 100% PKO-p or 100% *g*-PET. PU foam

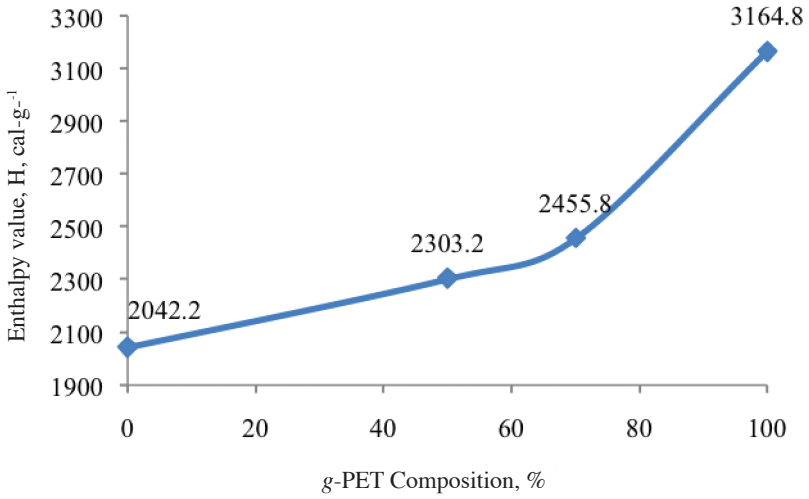

FIGURE 7. Initial enthalpy values of PU foam with the addition of 0, 50, 70 and 100% w/w *g*-PET

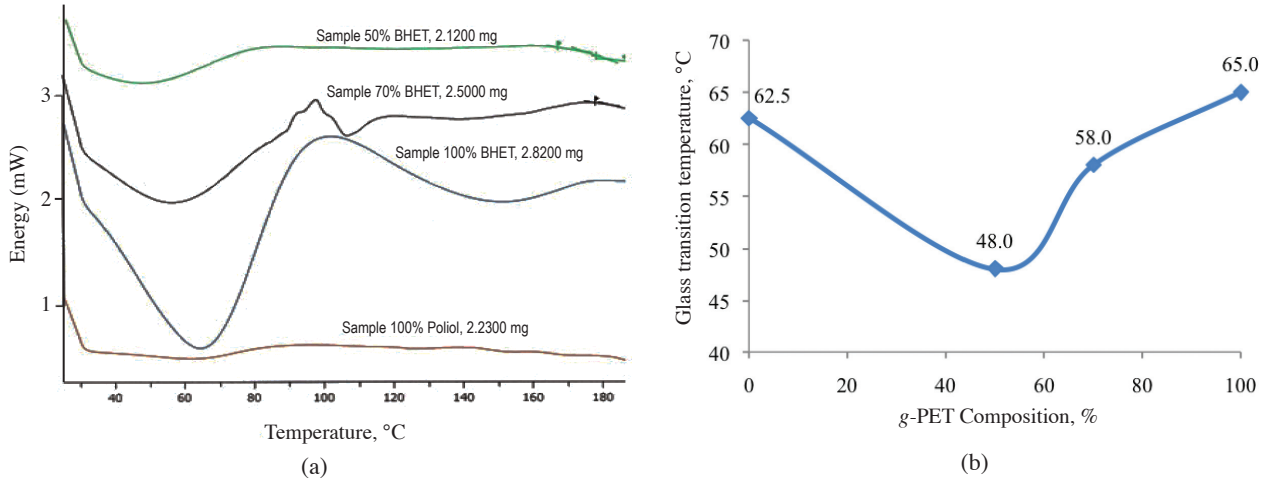

FIGURE 8. (a) DSC thermogram and (b) glass transition temperature, T_g of the PU foams with the addition of 0, 50, 70 and 100% w/w *g*-PET

with higher *g*-PET content has higher T_g. The NCO groups in MDI favor to react with active hydroxyl groups (PKO-p has carbamate –CN-$(ROH)_2$). Excess of MDI tend to react with less reactive OH groups offered by *g*-PET. However, this reaction always has the possibility of being interrupted by NCO reacted with free water molecules from PKO-p (due to its hygroscopicity) and surroundings contributing to poor chain rigidity (Cowie 1991) with lower T_g.

CONCLUSION

Rigid PU foam was prepared from glycolysed PET waste blended with palm-based monoester. 100% *g*-PET when converted to resin and reacted with MDI formed PU foam with high T_g and high compressive strength and modulus. This might provide an advantage in future planning for recycling of PET bottles as there is a potential for PU enhancement in mechanical and thermal properties with the inclusion of the former.

ACKNOWLEDGEMENTS

The authors would like to extend their gratitude to Universiti Kebangsaan Malaysia for providing the facilities and technical supports through this paper. This project was one of the finalists in the Innovation Competition for Commercialised Recycled Materials: 3R Innovation 2011 through the hard work conducted by Ms Ly Iliyana Mohd Dawi.

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Received: 8 June 2011
Accepted: 15 March 2012